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Lake Resources at Risk to Acidic Deposition in the Upper Midwest

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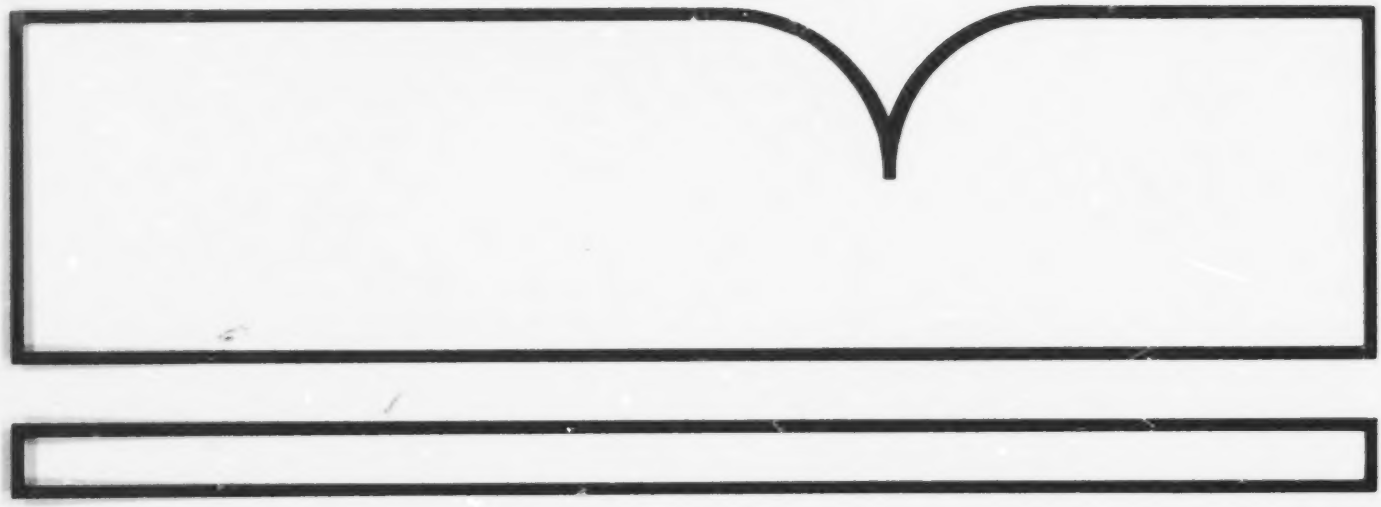

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16. ABSTRACT

The acidification of lakes and streams as a result of acid precipitation has been documented in southern Sweden and Norway,[1,2,3] the northeastern United States,[4,5] and southern Ontario.[6,7] Simple[8,9] and complex[10,11] models have been used to assess the impact of acidic deposition on lakes and streams. One model development[12,13,14] (the Trickle-down model) places particular emphasis on the kinetics of chemical weathering in the watershed as the primary mechanism that produces cations (Ca^{+2}, Mg^{+2}, K^{+}, Na^{+}) and neutralizes acid inputs.

In this study the Trickle-down model was used to simulate lake response and to predict the percentage of lakes in the Upper Midwest of the United States at risk at various levels of acidic deposition.

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Lake resources at risk to acidic deposition in the Upper Midwest

Jerald L. Schnoor, Nikolaos P. Nikolaidis, Gary E. Glass

The acidification of lakes and streams as a result of acid precipitation has been documented in southern Sweden and Norway,[1,2,3] the northeastern United States,[4,5] and southern Ontario.[6,7] Simple[8,9] and complex[10,11] models have been used to assess the impact of acidic deposition on lakes and streams. One model development[12,13,14] (the Trickle-down model) places particular emphasis on the kinetics of chemical weathering in the watershed as the primary mechanism that produces cations (Ca^{+2}, Mg^{+2}, K^{+}, Na^{+}) and neutralizes acid inputs.

In this study the Trickle-down model was used to simulate lake response and to predict the percentage of lakes in the Upper Midwest of the United States at risk at various levels of acidic deposition.

ACID LAKES IN THE UPPER MIDWEST

Site description. A large number of lakes (1000–2000) in the Upper Midwest are sensitive to acidic deposition. Sensitivity is defined here as any lake which has less than 40 μeq/L of alkalinity (acid neutralizing capacity). Surveys by the U. S. Environmental Protection Agency (EPA), Duluth Environmental Research Laboratory (ERL-D), and the Wisconsin Department of Natural Resources, Rhinelander, showed that 22 of 772 lakes sampled were acid lakes (alkalinity concentration less than zero). These surveys sampled less than 10% of the lakes in the northern portions of Minnesota, Wisconsin, and Michigan; many more acid lakes exist.

Four sites were studied in detail: Filson Creek, Minnesota; Lake Clara and Lake Vandercook, Wisconsin; and McNearney Lake, Michigan. Filson Creek watershed[13] is located in northeastern Minnesota at the southern edge of the Boundary Waters Canoe Area in the Superior National Forest, a second-growth forest of aspen, birch, spruce, and conifers. Bedrock is gabbroic, and exposed bedrock comprises 10 to 15% of the 24-km^2 drainage basin. Glacial drift deposits and Holocene surficial materials are generally less than 1.5 m thick. Filson Creek waters are highly colored.

Lake Clara lies in a relatively undisturbed watershed 10 km southwest of Rhinelander in northcentral Wisconsin. Lake Vandercook is located about 40 km north of Lake Clara, just north of Minocqua, Wisc. Like Lake Clara, it is an oligotrophic, clear-water lake. Both lakes are located over crystalline gneissic bedrock, but surficial glacial deposits are very thick (30 to 60 m), which essentially isolates the lakes from bedrock. Organic soils are generally thin and acidic, and glacial deposits have poor buffering capacity, and consist mostly of medium to fine quartz sand with only traces of feldspar and clay minerals. The region is forested with second-growth mixed stands of coniferous and deciduous trees.

Lake McNearney is located in the Upper Peninsula (U. P.) of Michigan about 50 km west of Sault Ste. Marie. The watershed is forested with spruce and coniferous vegetation and has acidic, podzolic soils. Characteristics of the three lakes are presented in Table 1.

Only a small fraction of sampled lakes are now acidic, but modelling studies predict that up to 30% of them may be sensitive to future increases in acid deposition.

Depositional gradient. The Upper Midwest has a distinct depositional gradient from west to east. The study areas and precipitation pH (wet only) are given in Figure 1.[15] The gradient extends from northeastern Minnesota, where the volume-weighted average pH of precipitation is 4.8 to 4.9 and no acid lakes have been discovered out of 290 sampled, through north-central Wisconsin, where the pH of precipitation is approximately 4.6 and 16 out of 429 lakes sampled were acidic (4%). Finally, the gradient extends to the eastern portion of the Upper Peninsula of Michigan, where the pH of precipitation is 4.3 to 4.4 and where 10 of 53 lakes sampled (19%) were quite acidic. Where precipitation is significantly acidic (pH ≦ 4.6), acid lakes are found along the depositional gradient. Where precipitation is not so acid, acid lakes have not been found.

Water chemistry methods. Lake sampling began in the fall of 1978 and continued through the summer of 1983. Aircraft was used for synoptic sampling and rapid sample transport. In-situ measurements and 4-L water samples were collected at the approximate lake center at a depth of 1 m. When temperature and conductivity profiles indicated gradients were present, samples were also collected at mid-depth and within 1 m of the bottom. Replicate samples were taken at every tenth site. At the end of each day, field lab measurements of pH and conductivity were made; aliquots for metal analysis were acidified to 0.2% with concentrated HNO_3; and subsamples were filtered for chlorophyll-a analysis and frozen for anion analysis. The remaining water was kept cold (on ice) and dark and transported daily to ERL-D for additional measurements of alkalinity, pH, conductivity, color, and turbidity according to U. S. EPA Methods for Chemical Analyses of Water and Waste 310.1, 150.1, 120.1, 110.2, and 180.1, respectively.[16] The water was also taken to a U. S. Forest Service (USFS) field laboratory at Winton, Minn., for nutrients analyses and chlorophyll-a analyses of the frozen filtrates. Anions were measured at ERL-D by ion chromatograph and alkalinity (acid neutralizing capacity, Gran endpoint) by titration. Metals were analyzed at the EPA Corvallis Environ-

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Table 1—Characteristics of Lakes Clara and Vandercook, Wisconsin and Lake McNearney, Michigan.

	Lake Clara	Lake Vandercook	Lake McNearney
Physiographic			
Surface area, ha	33.9	39.8	50.4
Watershed area, ha	112.0	129.7	198.5
Volume, $10^6 m^3$	1.53	1.71	2.2
Mean depth, m	4.5	4.3	4.4
Water quality			
pH	6.2	6.1	4.4
Alkalinity (Gran), μeq/L	35	20	−37
Conductivity, μS/cm	36	20	34
Color, PCU	10	5	25
Chlorophyll, μg/L	1.2	5.3	1.0
Acid precipitation			
pH	4.6	4.6	4.4
SO_4^{-2}, kg/ha·a	14	14	17

mental Research Laboratory (ERL-C) by atomic absorption and inductively coupled plasma emission spectrometry. The analytical data were subjected to extensive quality assurance procedures to determine precision and accuracy of the measurements and for errors in computer manipulation. Duplicate analyses were averaged with replicate samples to yield a single value for each chemical parameter of each lake.

Water chemistry. Bar diagrams of ionic composition for three of the more intensively studied lakes are presented in Figure 2. Omaday Lake (in the Filson Creek watershed[13]) is not very sensitive to additions of acidity because it has an average alkalinity of 162 μeq/L. Bicarbonate is the predominant anion that results from the CO_2 weathering of glacial deposits and gabbroic bedrock. (Note the high magnesium concentration caused by the dissolution of olivine, $MgFeSiO_4$.) The average sulfate concentration in Omaday Lake was 59 μeq/L and the average sulfate in precipitation at the Fernberg National Acid Deposition Program (NADP) station was 30 μeq/L during 1981 and 1982. The average dissolved organic carbon concentration in Omaday Lake was 19.2 mg/L, which accounted for approximately 60 μeq/L of organic anions in the ionic balance (Figure 2).

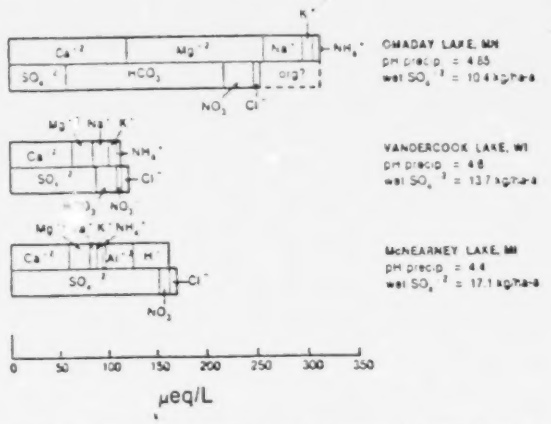
OMADAY LAKE, MN
pH precip. = 4.85
wet SO_4^{-2} = 10.4 kg/ha·a
VANDERCOOK LAKE, WI
pH precip. = 4.8
wet SO_4^{-2} = 13.7 kg/ha·a
McNEARNEY LAKE, MI
pH precip. = 4.4
wet SO_4^{-2} = 17.1 kg/ha·a
0 50 100 150 200 250 300 350
μeq/L

Figure 2—Comparison of water chemistry across the depositional gradient.

Vandercook Lake in Wisconsin is much more sensitive to acidic inputs than Omaday Lake, Minnesota. The average bicarbonate alkalinity was 21.5 μeq/L. Sulfate concentration in Vandercook Lake averaged 88 μeq/L compared with 35 μeq/L precipitation sulfate at the nearby Trout Lake NADP station from 1980 through 1982. The ratio of sulfate concentration in the lake to the sulfate concentration in the precipitation is an estimate of the evaportranspiration concentration factor, assuming sulfate behaves conservatively.

McNearney Lake in Michigan is a clearwater, acid lake that receives the highest sulfate and hydrogen ion concentrations across the depositional gradient. Although it had almost the same Ca^{+2} and Mg^{+2} concentrations as Vandercook Lake, the significantly higher sulfate concentration in McNearney Lake was balanced by aluminum and hydrogen ions; therefore, McNearney Lake is acidic and it has no fish.

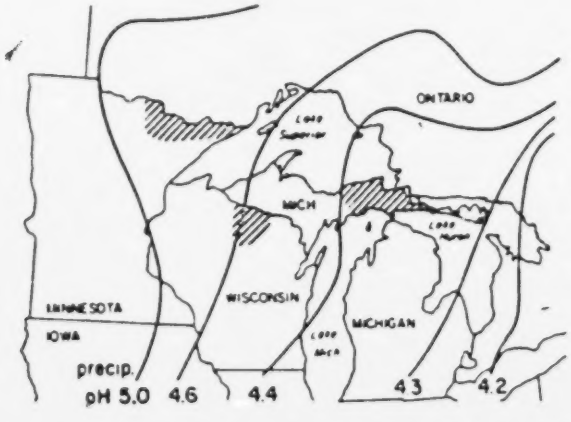

Figure 1—Study areas in northeastern Minnesota, northcentral Wisconsin, and the eastern portion of the Upper Peninsula of Michigan together with annual volume-weighted average pH of precipitation. Precipitation pH data were compiled from stations of the National Acid Deposition Program, the Canadian network, and EPA Region V, March 27, 1979 through April 1, 1980.

FACTORS CONTROLLING WATER CHEMISTRY

Geologic sensitivity. Lakes in all three study areas of the Upper Midwest have geologic sensitivity to acid deposition; that is, they have crystalline bedrock with thin overlying soils and surficial deposits with little acid neutralizing capacity (ANC). However, the bedrock is so deep in some areas, it is unimportant to the lake chemistry. Northeastern Minnesota has granitic bedrock with shallow, Quarternary deposits. Bedrock plays a large role in the chemistry and hydrology of the Minnesota lakes.[17] Northcentral Wisconsin has crystalline bedrock at a 30 to 60 m depth with low-ANC glacial deposits. The eastern portion of the Upper

Peninsula (U. P.) of Michigan has sedimentary (Cambrian, Ordovician, and Silurian) bedrock. The Cambrian red sandstones are believed to have low ANC but most of the other bedrock has high ANC. The bedrock is relatively deep (40 to 60 m) in the northern part of the area, and more shallow in the southern part. Thus, lakes in the northern portion of the study area tend to have the lowest alkalinity (Figure 3). Soils are quite acid in much of the northern U. P., which indicates that surficial deposits were derived from rocks with low ANC.

Hydrologic sensitivity. Juday and Birge[18] were the first to comment on the relationship between lake hydrologic type and specific conductance, and recent work by Eilers *et al.*[19] has related hydrology to lake alkalinity concentrations. Hydrologic sensitivity and lake type are defined by the presence of permanent surface water inlets and outlets (Figure 4). A lake with no inlets or outlets is classified as a seepage lake; a lake with only an inlet and no outlets is an inflow lake; a lake with both an inlet and an outlet is a drainage lake; and a lake with only a permanent outlet is a spring (spring-fed) lake. The most sensitive hydrologic type is the seepage lake, an idealized schematic of which is presented in Figure 5. Lakes Clara, Vandercook and McNearney are seepage lakes. Omaday Lake is a drainage lake.

Seepage lakes receive most of their water from precipitation that falls directly on the lake surface. Outflow is primarily by evaporation and, to a lesser extent, seepage into the groundwater. Thus, the lake chemistries are markedly influenced by precipitation chemistry. Seepage lakes occur in regions of thick glacial deposits, such as northcentral Wisconsin and the eastern U. P. of Michigan. There are approximately 9800 seepage lakes of the 14 252 lakes in Wisconsin alone.[20]

The most important factor that controls the ANC of lakes in a sensitive mineralogic region is their hydrology. Two types of sensitivity have been reported: flashy hydrographs, where water runs quickly through shallow, porous soils down steep slopes to the lake[12]; and seepage lakes.[19] In either case, the cause of sensitivity is the short residence time that water spends in deep soil while passing on its way to the lake.

A multivariate statistical analysis (discriminant analysis) was used to identify watershed variables that contribute to lake sensitivity in the U. P. of Michigan. The data base was compiled by Rapp *et al.*[21] Lakes were grouped into three clusters based on their average alkalinity: sensitive (<40 μeq/L), moderately sensitive (40–200 μeq/L), and nonsensitive (>200 μeq/L). It was possible to classify 62 to 89% of the lakes into the correct alkalinity cluster based on the following 12 watershed descriptors: hydrologic type, bedrock geology, depth to bedrock, number of outlets and inlets, maximum lake depth, site elevation, estimated lake residence time, precipitation and evaporation, percent forest type, and percent residential area within the watershed. Rank correlation coefficients indicated statistical significance at the $p \geq 0.05$ level. The watershed variables that indicated sensitivity to acid deposition were seepage-lake hydrologic type, large depth to bedrock, high site elevation, and a large percentage of the watershed in coniferous forest. The watershed variables that indicated non-sensitivity (high lake alkalinity) were drainage-lake hydrologic type, a large number of inlets, and a high percentage

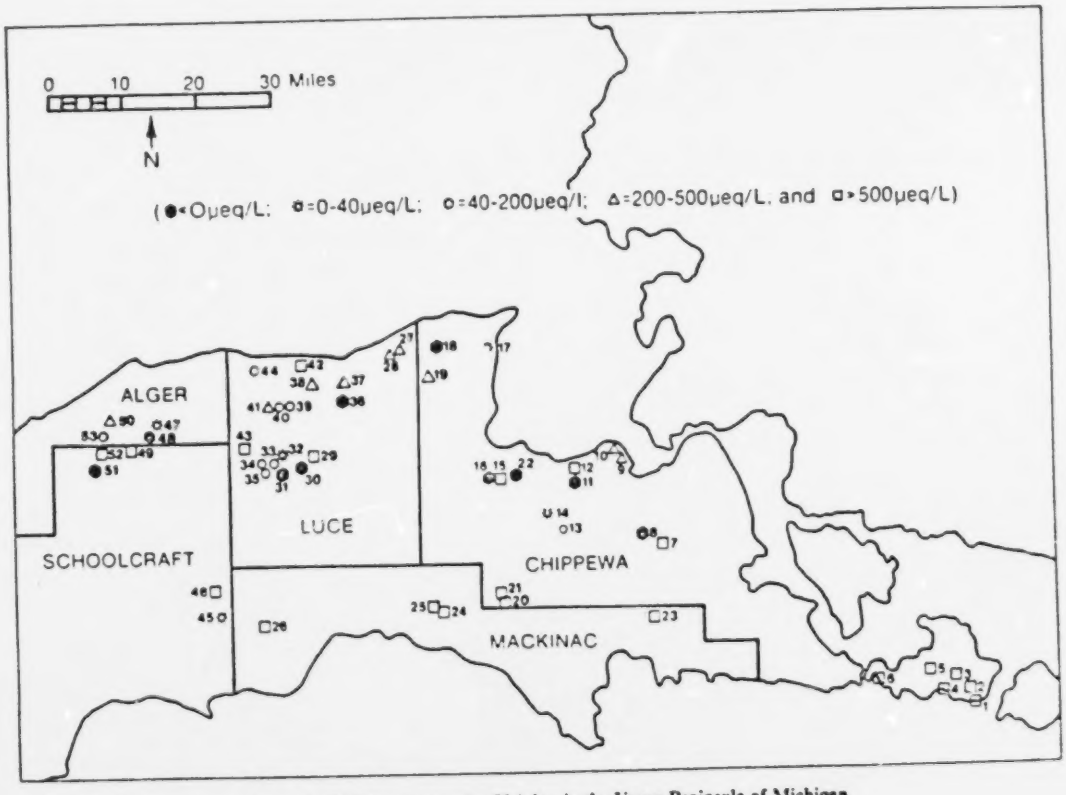

Figure 3—Distribution of sites and alkalinity clusters for 53 lakes in the Upper Peninsula of Michigan.

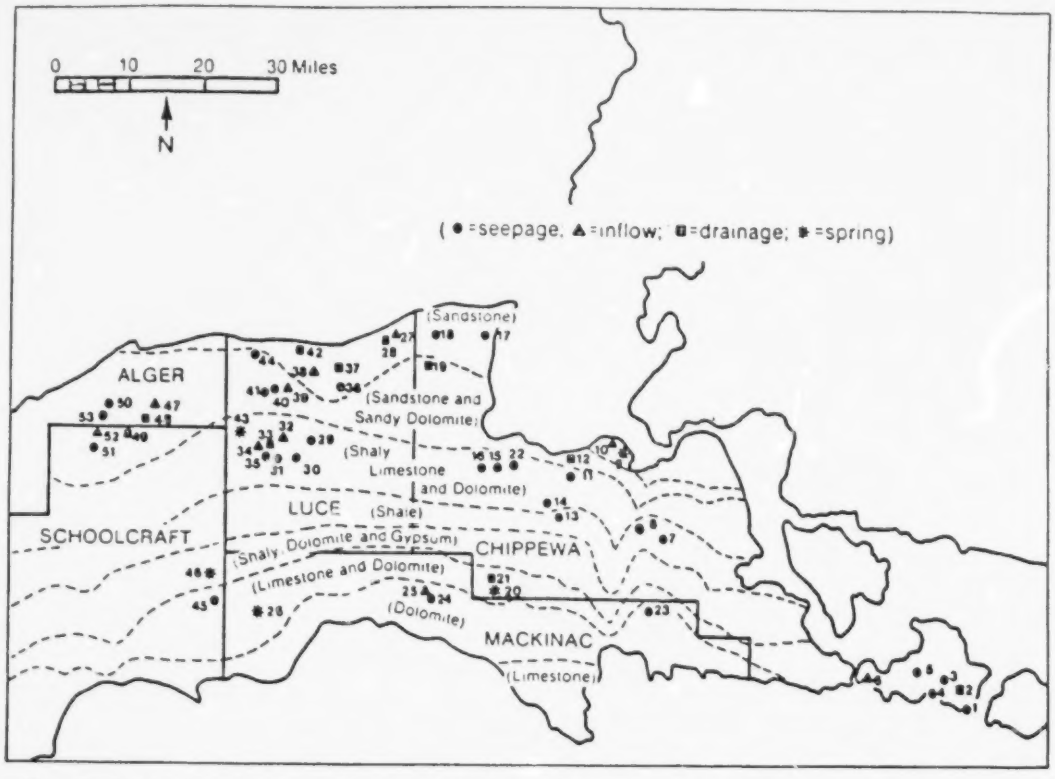

Figure 4—Distribution of sites, hydraulic type, and bedrock geology for 53 lakes in the Upper Peninsula of Michigan.

of the watershed in residential area. The factors that control alkalinity in these lakes involve hydrology, geology, and land use.

MODEL DEVELOPMENT

A compartmentalized, time-variable version of the Trickle-down model[13] and a steady state version[12,14] have been described previously. The model is based on a mass balance for alkalinity in the watershed and lake. A simple input/output analysis for a lake can be expressed mathematically as:

$$V\frac{d(Alk)}{dt} = -IL_{acy}(1-f) - Q(Alk) \qquad (1)$$

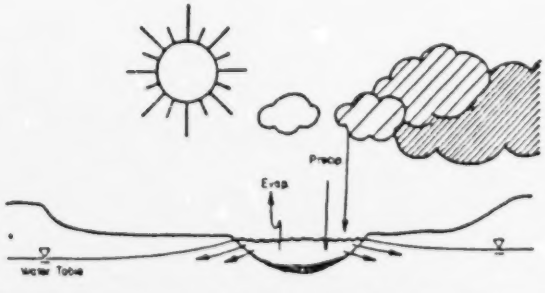

Figure 5—Schematic of a seepage lake with no inlets or outlets.

Where

V = water volume of the lake, m^3,
Alk = alkalinity concentration, μeq/L,
t = time, years,
I = total inflow volume per time, m^3/a,
L_{acy} = total acidity of precipitation (dry + wet), μeq/L,
Q = outflow or seepage rate, m^3/a, and
f = ratio of alkalinity produced in the watershed to the acid input.

A time-variable solution to Equation 1 is given in Equation 2.

$$Alk = A_0e^{-Qt/V} - \frac{I}{Q}L_{acy}(1-f)(1-e^{-Qt/V}) \qquad (2)$$

Where

A_0 = initial alkalinity concentration of the lake, μeq/L.

Under steady-state conditions, the alkalinity concentration in the lake is:

$$(Alk) = \frac{I}{Q}L_{acy}(f-1) \qquad (3)$$

The fraction of acidic deposition that is neutralized in the watershed can be defined in terms of a watershed weathering rate, W.

$$f = W/[RL_{acy}(0.1)] \qquad (4)$$

Where

W = weathering rate, eq/ha · a,
R = precipitation rate, cm/a,

L_{acy} = total acidity input, μeq/L, and
0.1 = units conversion factor.

The weathering rate should be considered as the total alkalinity production within the watershed by all processes (chemical weathering, ion exchange, and oxidation-reduction processes). Thus it is really a watershed neutralization rate. In most cases, the neutralization rate is predominantly caused by cationic exchange in soils and chemical weathering of minerals. To the extent that chemical weathering of minerals serves to replace exchangeable cations in the soil complex, chemical weathering is the rate-determining step that serves to neutralize incident acid precipitation. The net effect of chemical weathering is the consumption of H^+ and the release of basic cations (Ca^{+2}, Mg^{+2}, K^+, Na^+).

Stumm, *et al.*[22] showed that the rate of weathering of δ-Al_2O_3 is proportional to the degree of surface protonation and to the surface complexation of oxalate, {−Ox}, in laboratory experiments.

$$\text{Rate} = k_1\{-OH_2^+\}^3 + k_2\{-Ox\} \quad (5)$$

Where

Rate = the rate of dissolution of aluminum oxide,
$k_{1,2}$ = rate constants.

Equation 5 results in a dissolution rate that is proportional to the bulk phase $\{H^+\}$ to the 0.4 power. Many common minerals have been reported to undergo fractional order dissolution in acids, including dolomite, bronzite, enstatite, diopside, potassium feldspar, iron hydroxide, and aluminum oxide.[12]

An expression for chemical weathering (that is analogous to Equation 5) is:

$$W = k_h\left\{\frac{L_{acy}}{L_{ref}}\right\}^m + k_0 \quad (6)$$

Where

W = chemical weathering rate, eq/ha-yr,
L_{ref} = reference acidity concentration, μeq/L,
k_h = rate constant for acid hydrolysis, eq/ha-yr,
m = fractional order reaction rate constant, and
k_0 = rate constant in the absence of free acidity (due to CO_2 and ligand weathering), eq/ha-yr.

The fractional order kinetics of hydrolysis (Equation 6) have profound implications in terms of the response of ecosystems to acidic deposition. If $m = 0$, watersheds would have constant weathering (neutralization) rates, and increasing inputs of acid precipitation could not be neutralized. If $m = 1.0$, the soils and till would act as a perfect buffer, able to neutralize any inputs of acidity. Because fractional order kinetics apply ($0 < m < 1.0$), increases in acidic deposition are only partially compensated by increases in chemical weathering; therefore, an acid rain problem exists in lake watersheds with extreme hydrologic and geologic sensitivity that receive acidic deposition.

The alkalinity mass balance provides additional information on water chemistry. The basic cation concentration (Ca^{+2}, Mg^{+2}, K^+, Na^+), excluding sea salt or other neutral salts, is expected to be:

$$\{\text{Cation}\} = \left(\frac{I}{Q}L_{acy} + Alk\right) = WI/[RQ(0.1)] \quad (7)$$

and the acid anion concentration (SO_4^{-2}, NO_3^-, Cl^-), excluding neutral salts, is:

$$\{\text{Anion}\} = \frac{I'}{Q}L_{acy} \quad (8)$$

The partial compensation factor (F, defined by Wright and Henriksen[9]) can be calculated as

$$F = \frac{mk_h}{R(0.1)L_{ref}^m L_{acy}^{(1-m)}} \quad (9)$$

Equation 9 gives the change in cations or alkalinity with respect to the change in anion concentration (sulfate load). It defines sensitivity in terms of a lake's capacity to compensate additional acid inputs. It is variable during the lake titration process, and ranges from nearly 1.0 initially to 0.0 after all buffering capacity has been consumed.

Estimation of rate constants. The most difficult problem is how to derive the rate constants for Equation 6. An average fractional order hydrolysis constant for pure minerals in the laboratory is $m = 0.5$. Assuming $m = 0.5$, Equation 6 gives one equation with three unknowns (W, k_h, and k_0). The following parameter estimation procedure is recommended for cases in which historical water quality and precipitation acidity are not known. Current levels for acidic precipitation and lake alkalinity, inflow rate, outflow rate, and precipitation rate must be known.

1. Assume the current volume-weighted average precipitation acidity is equal to L_{ref}. This requires that dry deposition is minimal; otherwise, it should be added to the acidity of precipitation and included in L_{ref}. Also, the lake should be in approximate equilibrium with current acid loadings, and there should not have been recent changes in loadings. Nitrification of ammonia in precipitation, sulfide mineral oxidation, and biomass accretion are assumed to be negligible.

2. Calculate the current weathering (neutralization) rate, W_{ref}, based on recent measured lake alkalinity concentrations and precipitation rate.

$$W_{ref} = \left(\frac{I}{Q}L_{ref} + Alk\right)\cdot\left(\frac{RQ}{I}\right)\cdot(0.1) \quad (10)$$

3. Assume an F-factor at low acid precipitation loadings. For lakes in the Upper Midwest, $F \cong 1.0$ when $L_{acy} = 1$–10 μeq/L, based on Birge and Juday's measurements.[18] This assumption means that the lake was relatively well buffered when acid precipitation inputs were small. Calculate k_h, the mineral hydrolysis rate constant, based on the model parameters $F \cong 1.0$, $L_{acy} = 1$–10 μeq/L, and L_{ref} current precipitation acidity.

$$k_h = (FR(0.1)\sqrt{L_{ref}L_{acy}})/m \quad (11)$$

4. Solve for k_0, the non-hydrolysis rate constant which includes carbon dioxide and organic and inorganic ligand dissolution of minerals. Equation 12 is based on Equation 6 when $L_{acy} = L_{ref}$.

$$k_0 = W_{ref} - k_h \quad (12)$$

Once the rate constants are estimated, it is possible to combine Equations 3, 4, and 6 to solve for the lake alkalinity concentration at any acid loading concentration (L_{acy}) under steady-state conditions.

$$Alk = \frac{I}{Q}\left\{\frac{k_h\left(\frac{L_{acy}}{L_{ref}}\right)^m + k_0}{R(0.1)} - L_{acy}\right\} \quad (13)$$

Alkalinity in the lake is equal to the weathering products minus

Table 2—Water chemistry and weathering rates of northcentral Wisconsin lakes by hydrologic classification.

Classification	Conductivity μmhos/cm, 25°C		Total alkalinity μeq/L		pH		Weathering rate*	Number of determinations
	Median	Quartile range	Median	Quartile range	Median	Quartile range	eq/ha · a	
Rainwater	15	9-24	−25		4.6		—	75
Seepage lake	21	19-31	39	10-100	6.35	5.9-6.95	320	117
Inflow lake	36	31-55	160	135-200	6.9	6.8-7.15	660	9
Drainage lake	64	54-79	513	270-610	7.5	7.25-7.75	1700	106
Spring lake	74	63-92	588	425-670	7.7	7.5-8.0	1900	31
Groundwater	81	78-110	1100	650-2200	7.25	6.75-7.6	3300	72

* Weathering Rate is expressed in eq/ha · a of alkalinity produced by all processes.

the total acidity of precipitation, concentrated by an evapotranspiration factor (I/Q).

If the acidity of precipitation and the fraction of acid neutralized in the watershed are time-variable, then Equations 2, 4, and 6 can be used to develop the time-variable solution for any loading scenario.

RESULTS AND DISCUSSION

Hydrologic factors. Table 2 shows the marked effect of lake hydrologic type on lakes in northcentral Wisconsin. Seepage lakes are the most dilute waters with the exception of rainwater. At the opposite end of the spectrum for hydrologic sensitivity are spring-fed lakes that have chemistries rather similar to groundwater.

The degree of sensitivity varies among lakes within a given hydrologic class. Lakes that have no permanent inlets or outlets are not necessarily void of groundwater influence (as depicted in Figure 5). It is possible to have a seepage lake that has both groundwater inflow (recharge) and outflow to the groundwater (seepage). Figures 6-9 give the response of Lake Clara and Lake Vandercook to a very large storm event of June 1981. Both lake volumes increased after the storm and then gradually decreased

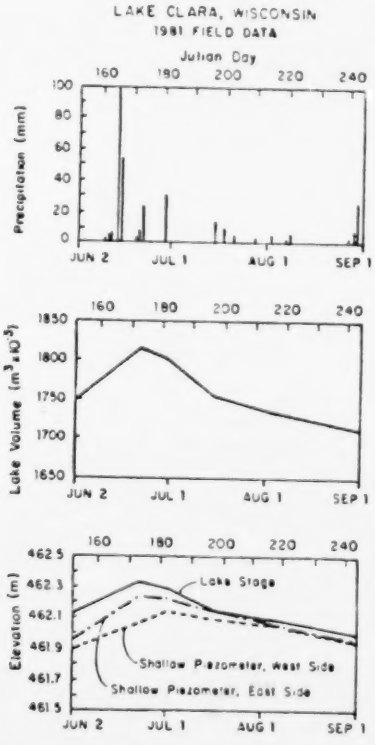

Figure 6—Lake Clara hydrologic response following a major storm in June 1981.

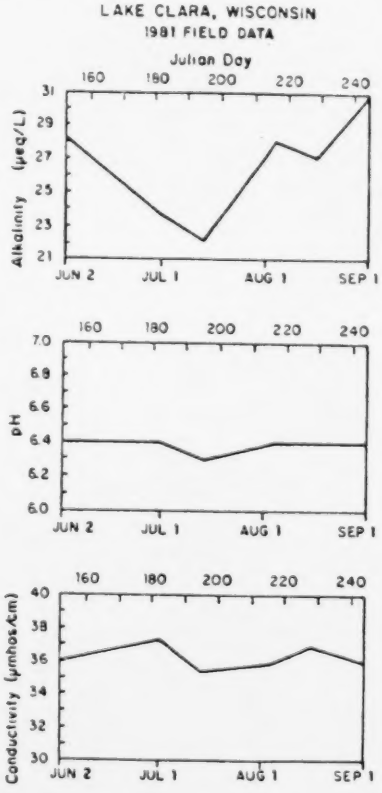

Figure 7—Lake Clara chemical response following a major storm in June 1981.

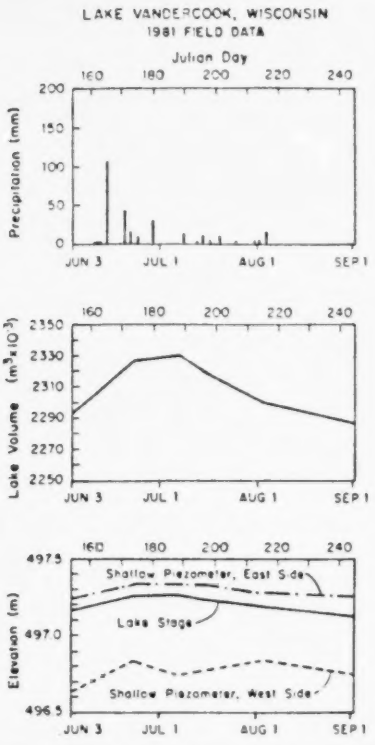

Figure 8—Lake Vandercook hydrologic response following a major storm in June 1981.

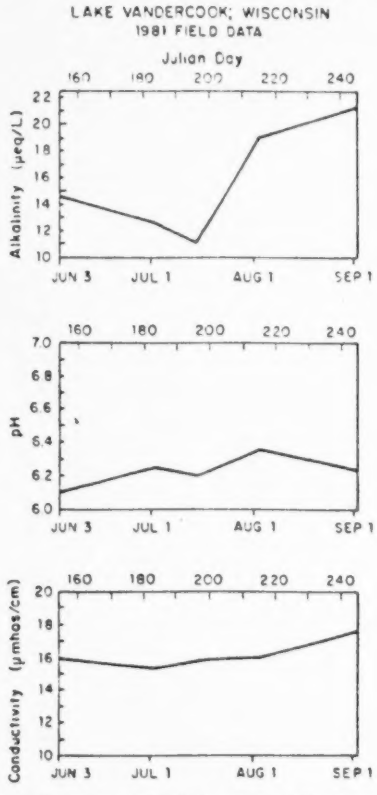

Figure 9—Lake Vandercook chemical response following a major storm in June 1981.

in an exponential function caused by seepage. In Lake Clara, most of the near-shore piezometers were continuously below the lake level, which indicates seepage to the groundwater, while in Lake Vandercook, the piezometers on the east side of the lake had groundwater levels slightly higher than lake level, which indicates some groundwater inflow to the lake.

The input of acidity from the storm was sufficient to decrease alkalinity somewhat (Figures 7 and 9), but the decrease was compensated later by weathering and internal processes (algal uptake of nitrate as well as sulfate reduction). pH was not a reliable indicator of lake alkalinity because of the diurnal swings with photosynthetic activity and CO_2 effects. Conductivity was extremely low in Lake Vandercook (Figure 9), almost equal to rainwater, but in Lake Clara, conductivity was significantly increased by road salting in the watershed.

Steady-state model. The model parameters for use in Equation 13 are given in Table 3. Hydrologic budgets (I, Q, R) were obtained from the United States Geological Survey for the Wisconsin lakes.[23] Figure 10 is a plot of the reaction pathway that each lake would follow once the lake obtained steady state with regard to each level of acidic deposition. Current field measurements for lake alkalinity and precipitation acidity are shown by the crosses in Figure 10. Lake alkalinity concentrations are slightly higher than Equation 3 predicts because the lakes are not quite at steady state with regard to current inputs of acidic deposition. The x-axis is the precipitation acidity (L_{acy}) multiplied by the evaporation concentration factor (I/Q). The pH scale is approximate and based on titration of bicarbonate alkalinity under atmospheric carbon dioxide levels. pH would differ somewhat under the influence of other weak bases (such as conjugate bases of organic acids or hydroxy-aluminum complexes).

Figure 10 indicates that Lake Clara is the least sensitive lake to acid deposition and Lake McNearney is the most sensitive. Calculations indicate that Lake McNearney became acidic at an acidity level (IL_{acy}/Q) of approximately 50 μeq/L which, with an evaporation concentration factor of 2.7, would have been a precipitation pH of 4.7. Lake McNearney is the most sensitive lake in the Upper Midwest that was sampled in this study. Lake

Table 3—Model parameters for Lakes Clara, Vandercook, and McNearney in Equations 2, 4 and 6.

Parameter	Lake Clara	Lake Vandercook	Lake McNearney
Acidity of precipitation (L_{acy}), μeq/L	27.8	30.0	40.0
Inflow, L/a	3.5×10^8	4.7×10^8	5.1×10^8
Outflow, L/a	1.1×10^8	1.6×10^8	1.9×10^8
Evaporation concentration factor (I/Q)	3.06	3.02	2.67
Detention time (V/Q), years	15.0	11.0	11.4
Precipitation rate (R), cm/a	86.3	68.7	76.0
Reference acidity (L_{ref}), μeq/L	5.0	5.0	5.0
Hydrolysis constant (k_h), eq/ha·a	110	107	45
Ligand constant (k_a), eq/ha·a	60	40	50
Fractional reaction order (m)	0.5	0.5	0.5

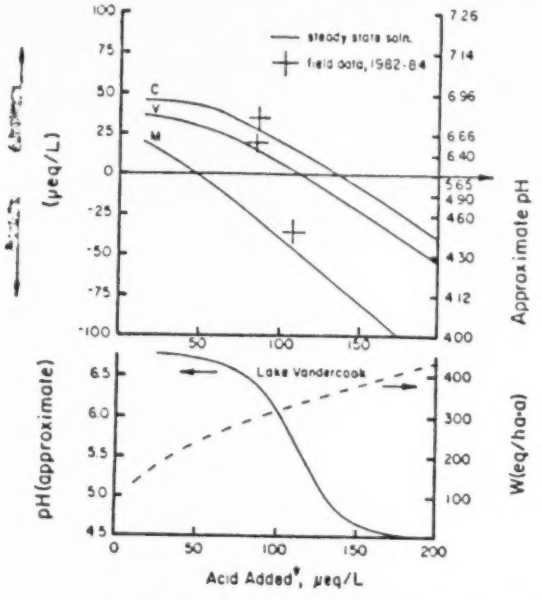

Figure 10—Steady-state model plot of alkalinity, pH, and chemical weathering rate versus the acidity of precipitation concentrated by evaporation (IL_{acy}/Q) in Lake Clara (C), Lake Vandercook (V), and Lake McNearney (M).

Clara is considerably less sensitive and, according to the results in Figure 10, would become acidic at a volume-weighted average precipitation pH of 4.4. Current values of precipitation pH are about 4.6 in northcentral Wisconsin, so a decrease in precipitation pH to that level would acidify Lake Clara and Lake Vandercook and a great many other lakes in the region.

Lake Vandercook is between Lake Clara and Lake McNearney in its response to acid precipitation. An example titration curve and weathering rate plot are shown in the bottom panel of Figure 10 for Lake Vandercook. Note that the weathering rate pathway is a curve with decreasing slope, which indicates declining partial compensation of acid inputs by chemical weathering. The F-factor of Equation 9 varies from $F \cong 1.0$ when $IL_{acy}/Q = 15$ μeq/L to $F = 0.42$ when $IL_{acy}/Q = 120$ μeq/L. The F-factor is much lower for Lake McNearney than for Lake Vandercook, and varies from 0.6 to 0.2 over the same range of acid precipitation loading.

Lake Clara, Lake Vandercook, and Lake McNearney have relatively long hydraulic detention times (V/I) of 4 to 5 years, but the residence times of alkalinity in the lakes (V/Q) are even longer (11 to 15 years). Alkalinity can be generated by in-lake processes but can also be consumed.[12] Thus the lakes take a long time to respond to changes in acidic deposition; roughly three alkalinity residence times are required to come within 95% of steady state.

Time-variable model. Equation 2 was used in conjunction with the steady-state Equations 4 and 6 to reconstruct the history of these lakes. First, a scenario for acid precipitation levels (L_{acy}) was projected based, in part, on sulfur dioxide emissions in the state.[24] Then the ratio of alkalinity produced in the watershed to the acid input (f) was computed for each L_{acy} using Equations 4 and 6. Finally Equation 2 was used to reconstruct the lake

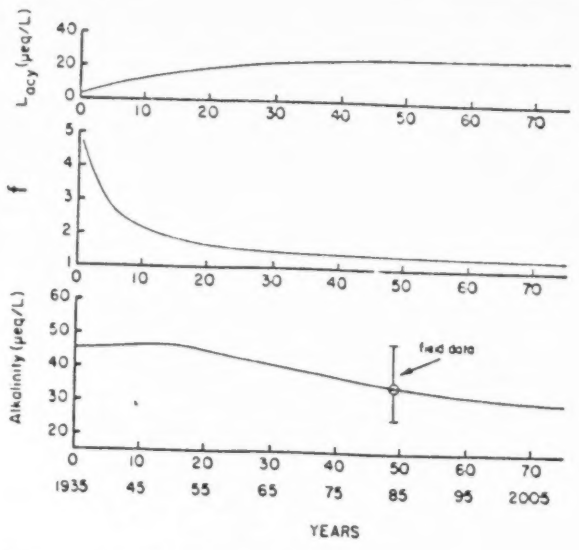

Figure 11—Lake Clara reconstructed lake history.

history. Figures 11–13 are the results. These results are consistent with what is known about these lakes, but since historical data do not exist for model verification, they should be considered only as experimental model simulations.

Birge and Juday measured the methyl-orange alkalinity of Lake Vandercook[18] to be approximately 70 μeq/L, which would indicate that the lake has become more acidic. If a correction is made for methodological differences between the methyl-orange and the Gran endpoint, the alkalinity of Lake Vandercook in the 1930s may have been as low as 6 μeq/L, which would indicate that the lake is presently more basic.[25] Data to determine whether or not the alkalinity concentration has changed significantly over the last 50 years is not yet available. The example demonstrates how difficult it is to determine trends for dilute lakes in the

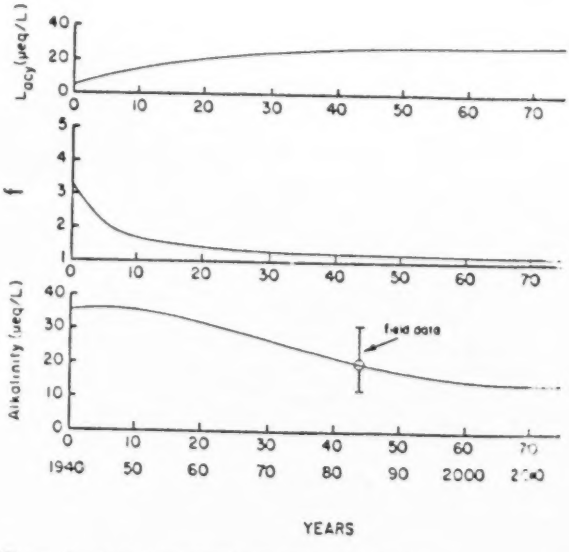

Figure 12—Lake Vandercook reconstructed lake history.

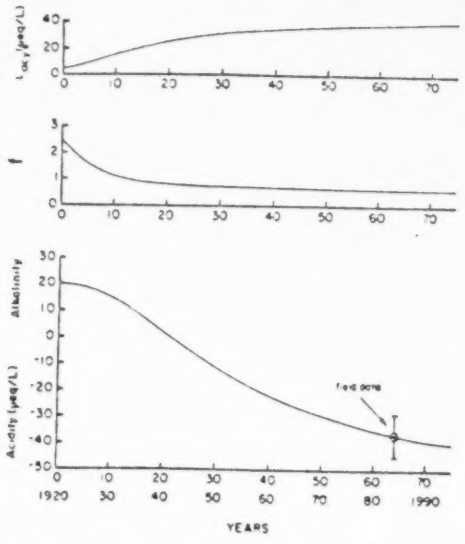

Figure 13—Lake McNearney reconstructed lake history.

absence of frequent and consistent measurements. In addition to the changes in acid loading (L_{acy}) to the lakes over time, one must know the changes in base loading over time. Since 1950, about 35 dwellings have been added to the shoreline of Lake Vandercook that have caused soil disturbances and the possible input of nutrients from septic tank absorption fields. Nutrient uptake of nitrate and phosphate by algae can add alkalinity to lake water.[12,14]

All of the lakes in Figures 11–13 are affected by the acidity input, but the decreases in alkalinity in Lake Clara and Lake Vandercook are on the same order as the variability in field measurements, so no conclusion as to their acidification can be reached. Lake McNearney has likely been acidified over a 50-year interval because of anthropogenic acidic deposition. This conclusion follows from its sensitive geologic and hydrologic setting and the high concentrations of sulfate in precipitation and in the lake (Figure 2).

Resources at risk. The steady-state model (Equation 13) was used to project the alkalinity of all the lakes that were sampled in northcentral Wisconsin and the eastern U. P. of Michigan. Tables 4 and 5 are the results. A two-fold increase in the precipitation acidity (from approximately pH 4.6 to 4.3) would cause an additional 7 to 24% of the Wisconsin lakes to become acidic. The uncertainty in predicting the percentage of acid lakes under a two-fold increase in the precipitation acidity is caused by the use of two different procedures. The low estimate was obtained using a regression model based on watershed descriptors to verify the model and to set the parameters k_0 and k_A. The high estimate was obtained using the alkalinity concentration of each lake to determine k_0 and k_A in a calibration mode, similar to the procedure previously described.

The U. P. of Michigan is a smaller lake resource than northcentral Wisconsin based on the number and surface area of lakes. A two-fold increase in loading (from approximately pH 4.4 to 4.1) would cause an additional 15% of the lakes to become acidic or about 98 lakes out of 650 in a five-county area. On the other hand, a two-fold reduction in the precipitation acidity (from pH 4.4 to 4.7) would increase the alkalinity to greater than zero in all cases. These extremely dilute lakes, where sulfate is the dominant anion, will respond to changes in the precipitation pH and the amount of sulfate deposition.

Table 4—Lake resources at risk for northcentral Wisconsin using Model Equation 13 (non-random sample, 429 lakes).

	Wet precipitation acidity (μeq/L)	Number of acid lakes (alkalinity ≤ 0)	Percentage of acid lakes (n = 429)
Present status (field data)	30	16	4%
Increased loading (estimated)	60	47–120	11–28%
Decreased loading (estimated)	15	2	0.5%

CONCLUSIONS

- A small fraction of lakes sampled in the Upper Midwest are presently acidic (0% in northern Minnesota, 4% in northcentral Wisconsin, and about 19% in the eastern part of the Upper Peninsula of Michigan). Field data and analysis suggest that these lakes have been acidified by acid deposition for the following reasons:
  a) Acid lakes are found only where there is significant acid precipitation (pH ≤ 4.6) across the depositional gradient.
  b) Acid lakes are mainly (88%) seepage type lakes that receive most of their water from precipitation falling directly on the surface of the lake and have no permanent inlets or outlets.
  c) Sulfate is the dominant anion in precipitation and in the chemistry of these lakes.
  d) Mass balance calculations at calibrated watersheds (Lake Clara and Lake Vandercook) indicate that more than 90% of hydrogen ions come directly from precipitation.
- The Upper Midwest is sensitive to future increases in acid deposition. At the precipitation pH found in the Adirondack

Table 5—Lake resources at risk for the eastern end of the Upper Peninsula of Michigan using Model Equation 13 (non-random sample, 53 lakes).

	Wet precipitation acidity (μeq/L)	Number of acid lakes (alkalinity ≤ 0)	Percentage of acid lakes (n = 53)
Present status (field data)	45	10	19%
Increased loading (estimated)	90	18	34%
Decreased loading (estimated)	22.5	0	0%

Mountains of New York (pH 4.1), about 30% of the lakes would be acidified based on model predictions.

• The model described here is based on a mass balance for alkalinity in a lake. It was calibrated with field measurements, and the kinetic formulations were based on laboratory experiments reported in the literature on chemical weathering. The model can be used in a steady-state or a time-variable mode to yield the response to scenarios of increasing or decreasing acid deposition. It is a tool that may be used to estimate the lake resources at risk at various levels of acidic deposition.

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